Aircraft Measurement of PANs During TexAQS 2006

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Introduction:

Measurements of the PAN compounds on board of NOAA P3 during TexAQS 2006 were made using a Thermal Dissociation – Chemical Ionization Mass Spectrometer (CIMS)[1], based on the following ionization mechanism[2,3]:

$$RC(O)OONO_2 + \Delta H \rightarrow RC(O)OO + NO_2$$
$$RC(O)OO + I^- \rightarrow RC(O)O^- + IO$$
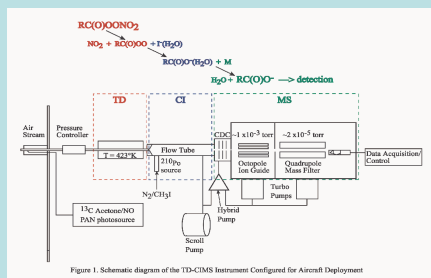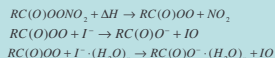$$RC(O)OO + I^- \cdot (H_2O)_n \rightarrow RC(O)O^- \cdot (H_2O)_n + IO$$

Figure 1. Schematic diagram of the TD-CIMS Instrument Configured for Aircraft Deployment

7 different PANs species (PAN, PPN, PiBN, MPAN, MoPAN, APAN, PBzN) plus 3 house keeping ion signals were recorded sequentially within a 2 second interval. The precise sampling time for each ion is known to a precision of a few milliseconds, but to avoid confusion, we reported them all on a 2 second time base. The exact time is provided upon request. The signal from each species has an averaging time of 150~200 milliseconds. Total measurement uncertainty is ~15%.

Calibration is done by continuously injecting a known amount of isotopically labeled PAN into the inlet. The latter is produced from the reaction of a small, accurately measured flow of an NO calibration standard with an excess of photochemically generated peroxyacetyl (PA) radicals from the 285nm photolysis of $^{13}C_3$ acetone in the presence of O_2[4]. The NO is efficiently converted first to NO_2, then to PAN.

NOTES:

Long chain carboxylate ions undergo fragmentation in the heated inlet. For PnBN, only ¼ of the total ions remained as $CH_3(CH_2)_2C(O)$ O-. Since, in the atmosphere, the concentration of PnBN is low compared to PiBN, all butyl peroxy nitrates are reported as PiBN.

Laboratory tests showed that a large fraction of PBzN irreversibly sticks to the inlet walls. We could not determine a reproducible transmission rate.

Statistics of the PANs measurements on board of NOAA P3 during TexAQS 2006:

Table 1. Summary of [PANs] observed during TexAQS 2006

	Average	Median	Maximum	Minimum
[PAN], pptv	552.7	449	5110.6	11.8
[PPN], pptv	85.4	60.1	960.8	0.6
[PiBN], pptv	18.1	13.1	196.3	0.7
[MPAN], pptv**	23.3	18.4	302.9	2.5
[MoPN], pptv	8.83	6.6	79.8	1.1
[APAN], pptv	15.6	11.4	302	1

**MPAN has a very large measurement uncertainty (~75 %) due to calibration problems

Table 2. Summary of PANs to PAN Ratios

	PPN/PAN	PiBN/PAN	MPAN/PAN	MoPN/PAN	APAN/PAN
Avg.	16.5%	2.9%	2.3%**	0.6%	2.3%
Max.	21%	4%	3.7%**	1.2%	14%
Min	7.8%	1.6%	1%**	0.1%	1.6%
All Data	17.3%	3.2%	2.9%**	1%	2.6%
2000 La Porte[5]	15.8%	3.3%	---	---	3.3%
2000 Electra	13.8%	2.0%	2.3%	---	2.3%

APAN observations during TexAQS2006:

Large mixing ratios of APAN were observed in Houston during TexAQS 2000 as reported by Roberts et al.[5]. The direct atmospheric precursor of APAN is 1,3-butadiene and acrolein, which in turn is formed from 1,3-butadiene . Large point sources of Butadiene from the petrochemical industry make APAN a very unique PAN compound for Houston.

The average APAN/PAN ratio we measured on board the P3 during TexAQS 2006 is about 2.6%, very similar to what was observed on the Electra in 2000, but expectedly a little bit lower than the 3.3% measured by GC in 2000 at La Porte, a ground site located near the ship channel.

Fig.2 shows an example of an APAN episode observed downwind of the Texas PetroChemicals LP plant, a large point source of 1,3-butadiene and ethene, on Oct. 6. The aircraft intercepted the plume 5 times at increasing distances downwind. The chemistry in this plume is explored here.
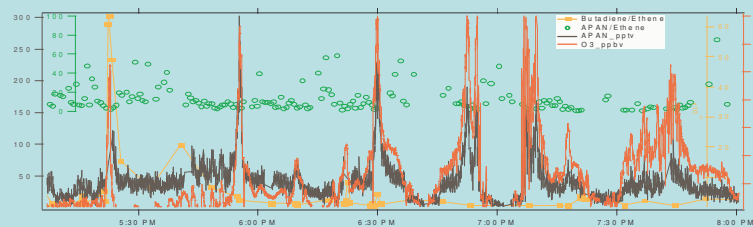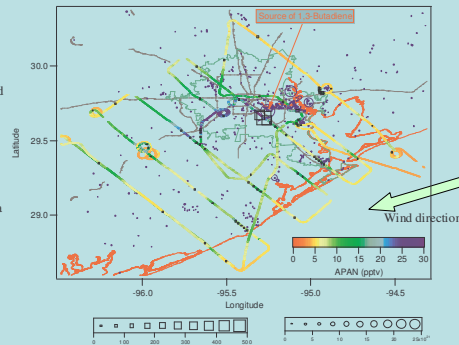

Fig 3. Time series of APAN and the ratios of 1,3-butadiene and APAN to ethene. Because ethene and APAN have approximately the same life time, the constant APAN/ethene ratio across the sharp plume peaks indicates that no other emissions blended in during transport. The formation of APAN (and therefore ozone) from 1,3-butadiene is very rapid. Almost all the 1,3-butadiene is depleted between the first and the second pass (37 km apart downwind of ship channel, corresponding to ~2 hours of transportation time). The APAN mixing ratios downwind of the second pass are therefore only affected by dilution and chemical loss.
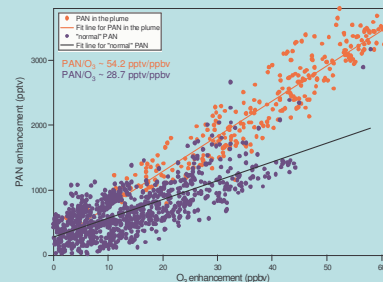

$PAN/O_3 \sim 54.2$ pptv/ppbv
$PAN/O_3 \sim 28.7$ pptv/ppbv

Fig4. shows the PAN enhancement versus O_3 enhancement during the APAN episode. The red dots represent samples where the APAN mixing ratio is larger than 85pptv, while the blue dots are the rest.

During the first pass downwind of the plant, ethene was 6 ppb and 1,3-butadiene was 500 ppt. This results in about the same overall OH reactivity.

The observed in-plume ozone to PAN ratio of about 19 is somewhat larger than what we observed previously in urban or power plant plumes with vigorous ozone production (ratios of 12-15). This is likely due to ozone produced from ethylene and 1,3-butadiene, which both do not produce PAN.

The even lower slope for the blue points is likely due to PAN loss through thermal decomposition as these air masses are not as productive as the petrochemical plume.

Assuming similar thermal losses and dilution, the decrease of the APAN/PAN ratio observed in the plume (shown in figure 5) can be used to estimate average OH mixing ratios as aircraft data for the radicals was not available for this flight. Due to the fast depletion of 1,3-Butadiene, APAN is no longer produced while other hydrocarbons still contribute to PAN and O_3 formation.

The time dependent APAN/PAN ratio can be expressed as:

$$R(t) = \frac{[APAN]_e}{[PAN]_e} = \frac{[APAN]_0 \exp(-k[OH]t)}{[APAN]_0 / R(0) + \Delta[PAN]_e}$$
$$[APAN]_e = [APAN] - [APAN]_{Background}$$
$$[PAN]_e = [PAN] - [PAN]_{Background}$$
$$k \approx 0.9 \times 10^{-11} - 1.1 \times 10^{-11} cm^3 / s$$

The correction for PAN production is obtained from the observed ozone enhancement, using the small slope in Fig 4. The fit gives a lifetime of APAN vs. OH reaction of 650 mins. Assuming a similar OH reaction rate as that for ethene (as inferred from MPAN), this corresponds to an average OH concentration of 2~3·10⁶ cm⁻³

Summary

- Several PAN species have been measured on board the NOAA P-3 during TexAQS 2006, with a time resolution of two seconds using the new compact PAN Thermal Dissociation - Chemical Ionization Mass Spectrometer.
- An APAN episode downwind of a strong point source of 1,3-butadiene (Texas PetroChemical LP) was observed on October 6th, 2007, downwind of the ship channel. 1,3-Butadiene was converted to APAN very rapidly.
- 1,3-butadiene and ethylene contributed ozone production significantly in this plume.
- The lifetime of APAN against OH reaction is about 10hours, resulting in an estimated average OH mixing ratio of 2~3·10⁶ cm⁻³ in this plume, which is a reasonable value for the conditions.

References:

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